Synthesis and Pyrolysis of Thermosetting Copolymer of Polysilastylene and Perhydropolysilazane

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熱硬化性ポリシラスチレン-ペルヒドロポリシラザン共重合体の合成と熱分解

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Copolymer of polysilastylene and perhydropolysilazane was obtained by the reaction of polysilastylene with zirconium *n*-butoxide and perhydropolysilazane. Zirconium *n*-butoxide and perhydropolysilazane were essential to render the thermosetting property. The thermosetting copolymers were converted into silicon carbide-based ceramics by pyrolysis at 1000°C in a stream of N₂ with about 80 mass% ceramic yield. The main phase of the pyrolysis product at 1500°C in N₂ was small crystallite β -SiC. Free carbon, based on rule-of-mixtures composition in the final ceramics could be reduced by varying the ratio of polysilastylene/perhydropolysilazane. The copolymer was dry spun and pyrolyzed to produce a ceramic fiber. Pyrolysis in N₂ at 1500°C yielded a silicon carbide-based fiber. Tensile strength of 1.0 GPa and elastic modulus of 190 GPa were obtained for the fiber from 10 to 12 μ m in diameter. Crystallization to α -Si₃N₄, β -Si₃N₄, β -SiC, and ZrN proceeded on annealing in N₂ at 1700°C for 1 h.

Key-words : Silicon carbide, Polymer, Pyrolysis, Zirconium, Silazane, Thermosetting

1. Introduction

Silicon carbide is a well-known ceramic material with high thermal and chemical stability, high mechanical strength and hardness, and high thermal conductivity. There has been much interest in the use of organosilicon polymers as precursors to silicon carbide-based ceramics. Some of the advantages in the preparation of ceramic materials from these precursors include compositional homogeneity in the final products, high purity ceramic products with uniform microstructure, amorphous to microcrystalline, and the preparation of refractory ceramics at relatively low temperatures.

Yajima and his co-workers¹⁾ developed polycarbosilane by thermal rearrangement of polydimethylsilane. Continuous SiC filament has been produced via pyrolysis of melt-spun polycarbosilane.²⁾ Babonneau and Soraru³⁾ reported the structure and the pyrolysis process of polyzirconocarbosilane which was prepared from polycarbosilane and zirconium *n*-butoxide. West et al.⁴⁾ prepared "polysilastylene"

by Na reduction of mixtures of Me₂SiCl₂ and PhMeSiCl₂. Polysilastylene is soluble in organic solvents and can be softened to viscous liquids at high temperatures. This polymer can be converted directly to silicon carbide, without prior conversion to a polycarbosilane. Ijadi-Maghsoodi et al.⁵⁾ demonstrated that silylene-acetylene could be synthesized by the reaction of dialkyl- or diaryldichlorosilanes with dilithioacetylene. These precursors were converted to silicon carbide-based ceramics by pyrolysis in inert atmosphere. However, curing process such as heat treatment in air, UV irradiation, and electron beam irradiation was essential for the preparation of shaped-SiC from thermoplastic precursors.

Several authors reported thermosetting SiC precursors. Schilling⁶⁾ described vinylic polysilane by refluxing various chlorinated silanes in a solvent with sodium. This vinylic polysilane was a viscous, liquid polymer that underwent thermal cross-linking in an inert atmosphere due to a combination of hydrosilylation and vinyl polymerization. Whitmarsh and Interrante⁷⁾ reported hydridopolycarbosilane derived from (chloromethyl) trichlorosilane that underwent facile thermal cross-linking reactions. Wu and Interrante⁸⁾ prepared poly (silaethylene) by direct reduction of poly (dichlorosilaethylene) that was obtained via ring-opening polymerization of 1,1,3,3-tetrachloro-1,3-disilacyclobutane. The presence of Si-H bonds in the polymers provided an effective thermosetting property. Toreki et al.⁹⁾ produced silicon carbide fibers by pyrolysis of dry spun polycarbosilane without curing process. Molecular weight of polycarbosilane was controlled by separation of low molecular weight thermoplastic carbosilane.

We have described¹⁰⁾ the production of thermosetting SiC precursor by copolymerization of polycarbosilane with thermosetting perhydropolysilazane. This paper describes the synthesis of thermosetting preceramic polymer by copolymerization of polysilastylene with perhydropolysilazane. Thermal cross-linking of perhydropolysilazane, below the softening point of polysilastylene, was expected to render thermosetting property to the product

copolymer. Properties of pyrolysis products as well as preliminary obtained ceramic fiber will be presented.

2. Experimental procedure

2.1 Preceramic polymer synthesis

Perhydropolysilazane (PHPS) was synthesized by ammonolysis of dichlorosilane-pyridine adduct followed by heat treatment at 120°C in pyridine with ammonia.¹¹⁾

Commercially available polysilastyrene (PSS, Nippon Soda Co., Ltd., PSS-400) with number average molecular weight of 1300 was used in this study. The procedure is close to the one used by Yajima to prepare the Ti-modified polycarbosilane.¹²⁾ PSS and zirconium *n*-butoxide in given ratio (Si/Zr=25/1 (atomic ratio)) were dissolved in xylene to form a homogeneous solution. The solution was refluxed under N₂ for 1h. After the refluxing reaction, the temperature was raised to 220°C and the xylene solvent was distilled off. The heat treatment was carried out at 220°C for 30 min. After being cooled to room temperature, the product was dissolved in xylene. PHPS in xylene was added to the yellow solution in given ratios (PSS/PHPS=2/1, 1/1, 1/4, 1/6 (Si ratio)). The mixture was heated at 100°C under N₂ for another 1h. The solvent was removed by vacuum distillation over a rotary evaporator to give light yellow powder.

2.2 Pyrolysis

Polymer samples were pyrolyzed in a carbon furnace (Model HG-010, Nikkato, Osaka, Japan) by heating from room temperature to 1500°C for 150 min, holding at 1500°C for an additional 60 min, and cooled to room temperature in 150 min. All heating was completed under a stream of N₂.

2.3 Characterization

Infrared (IR) spectra were recorded on polymer-coated KBr plates (Model 270-50, Hitachi, Tokyo, Japan). ¹H (Model R-24B, Hitachi, Tokyo, Japan) nuclear magnetic resonance (NMR) spectra were recorded for the polymers in CDCl₃ solutions at room temperature. Elemental analyses for Si, N, Zr, C, O and H were obtained for the polymers and pyrolyzed samples. Differential scanning calorimetry (DSC) was carried out in N₂ up to 500°C at a heating rate of 50°C/min (Model DSC 7, Perkin-Elmer, Norwalk, U.S.A.). Thermogravimetric analysis (TGA) was performed on the polymer up to 1000°C under a stream of N₂ (Model TG8110D, Rigaku, Tokyo, Japan) at a heating rate of 5°C/min.

X-ray diffraction (XRD) measurements were performed on the pyrolyzed samples with Cu K α radiation using an automated powder diffractometer equipped with a monochromator (Model RINT 1400, Rigaku).

X-ray photoelectron spectroscopy (XPS) was carried out with Mg K α (1253.6 eV) radiation as the excitation source (Model 5600 CI, Perkin-Elmer). The

analysis was performed, under a residual pressure at 6.66×10^{-8} Pa, on ground ceramic fibers. The XPS data recorded on the samples were calibrated utilizing the Si 2p binding energy in SiC (100.4 eV as standard).

2.4 Fiber preparation

Polymer solutions were filtered to remove insoluble material and concentrated to develop appropriate rheological characteristics for the spinning operation. Polymer fibers were continuously prepared by dry spinning at about 50°C. With proper drawdown of the viscous polymer solution during extrusion from the spinneret, fibers with diameters of 12–15 μ m were produced. A drum on a variable speed motor was used for fiber takeup. Polymer fibers (120 mm in length) were pyrolyzed in an Al₂O₃ tube furnace (Model F-1201, Nishimura Kogyo, Tokyo, Japan) under a stream of N₂ at 5°C/min to 1000°C, holding at that temperature for 1h. The pyrolyzed fibers were subsequently annealed for 1h under flowing N₂ at 1500°C in a carbon furnace (Model HG-010, Nikkato, Osaka, Japan).

3. Results and discussion

3.1 Characterization of copolymers

The IR spectrum of PSS (as-received) is shown in Fig. 1(A). The absorptions at 2900–3080 cm⁻¹ (C–H), 2100 cm⁻¹ (Si–H), 1350–1450 cm⁻¹ (C–H), 1250, 1420 cm⁻¹ (Si–CH₃), 1440, 1100, 740, 700 cm⁻¹ (Si–Ph), 1040 cm⁻¹ (Si–CH₂–Si), and 800 cm⁻¹ (Si–C) are observed. The absorption at 2100 cm⁻¹ (Si–H) indicate that PSS was heat-treated and contains some carbosilane structures. The ratio of the intensity of the absorption of Si–H bond at 2100 cm⁻¹ to that of Si–CH₃ bond at 1250 cm⁻¹ is 0.512. The equivalent ratio for the reaction product of PSS with zirconium *n*-butoxide is 0.440. This shows that some of the Si–H bonds in PSS disappeared during

Fig. 1. IR spectra of (A) PSS, (B) PSS/zirconium *n*-butoxide (Si/Zr=25/1), (C) PHPS, and (D) PSS/zirconium *n*-butoxide/PHPS (Si/Zr=25/1, PSS/PHPS=1/4).

the reaction. The bonding between PSS and zirconium *n*-butoxide might be Si–O–Zr. A small band at 480 cm⁻¹ in Fig. 1(B) can be assigned to Zr–O.³⁾ ¹H NMR spectrum of PSS (as-received) reveals three peaks at 0.4 ppm (SiCH₃), 4.5 ppm (weak; SiH), and 7.3 ppm (SiPh) (Fig. 2(A)). ¹H NMR spectrum of the reaction product of PSS with zirconium *n*-butoxide shows four new peaks at 0.95, 1.4, 1.6 ppm (CH), and 3.7 ppm (weak; OCH₂) (Fig. 2(B)). Zirconium *n*-butoxide can be incorporated as pendant substituents as the silicon sites of PSS. DSC curves of PSS (as-received) and the reaction product of PSS with zirconium *n*-butoxide show an endothermic peak starting at 210°C, with a peak maximum at 230°C (Figs. 3(A) and (B)). These curves suggest

Fig. 2. ¹H NMR spectra of (A) PSS, (B) PSS/zirconium *n*-butoxide (Si/Zr=25/1), (C) PHPS, and (D) PSS/zirconium *n*-butoxide/PHPS (Si/Zr=25/1, PSS/PHPS=1/4).

Fig. 3. DSC curves of (A) PSS, (B) PSS/zirconium *n*-butoxide (Si/Zr=25/1), (C) PHPS, (D) PSS/PHPS (PSS/PHPS=1/4), and (E) PSS/zirconium *n*-butoxide/PHPS (Si/Zr=25/1, PSS/PHPS=1/4).

that PSS and the reaction product of PSS with zirconium *n*-butoxide melt around this temperature.

The IR spectrum of PHPS (Fig. 1(C)) shows absorptions at 3400 cm⁻¹ (N–H), 2150 cm⁻¹ (Si–H), 1180 cm⁻¹ (N–H), and 840–1020 cm⁻¹ (Si–N–Si). The ratio of the intensity of the absorption of N–H bond at 3400 cm⁻¹ to that of Si–H bond at 2150 cm⁻¹ is 0.309. The equivalent ratio for the reaction product of PSS/zirconium *n*-butoxide with PHPS (Si/Zr=25/1, PSS/PHPS=1/4) (Fig. 1(D)) is 0.387. This indicates that cleavage of some Si–H bonds in PHPS occurred during the reaction of PHPS with PSS/zirconium *n*-butoxide. ¹H NMR spectrum of PHPS (Fig. 2(C)) reveals three peaks at 1.4 ppm (NH), 4.4 ppm (SiH₃), and 4.85 ppm (SiH/SiH₂). The ratio of the intensity of the signal of SiH₃ at 4.4 ppm to that of SiH/SiH₂ at 4.85 ppm is 0.328. The equivalent ratio for the reaction product of PSS/zirconium *n*-butoxide with PHPS is 0.296. The decrease of the amount of SiH₃ units in PHPS indicates that the reaction proceeded predominantly at these units in PHPS. The product copolymer might have some Si (PSS)–O–Zr–O–Si (PHPS) bondings. The DSC curve of PHPS (Fig. 3(C)) has exothermic peaks around 210°C and 250°C due to dehydrogenation of Si–H and N–H bonds. Thermal cross-linking around 210°C was expected to render thermosetting property to the copolymer. There is no endothermic peak around 230°C in the DSC curve of the product copolymer (Fig. 3(E)). This indicates that the product copolymer is thermosetting as expected.

Babonneau and Sorarú described³⁾ that no evidence for the presence of Si–O–Zr bonds could be found in the reaction product of polycarbosilane with zirconium *n*-butoxide. From the spectroscopic results of our polymers, there was no new signal observed for the presence of bondings between PSS and PHPS through zirconium *n*-butoxide. However, cleavage of the Si–H bonds in both PSS and PHPS occurred during the reaction. This might suggest the formation of Si–O–Zr bonds. Furthermore reaction product of PSS with PHPS (PSS/PHPS=1/4) without zirconium *n*-butoxide shows an endothermic peak around 230°C in the DSC curve (Fig. 3(D)). Zirconium *n*-butoxide was found to be essential for the polymer to show thermosetting property. This indicates that some bondings in the copolymer are necessary to show thermosetting property. Elemental analysis and DSC results for the polymers with varied PSS/PHPS ratio are summarized in Table 1. On

Table 1. Elemental Analysis and DSC Results of Copolymers with Different PSS/PHPS Ratios [(Total Si)/Zr=100/1]

PSS/PHPS (Si ratio)	Composition (mass%)							Endothermic peak at 230°C in DSC curve
	Si	N	Zr	O	C	H		
2/1	40.70	7.88	1.33	2.64	39.60	7.85		yes
1/1	43.40	12.60	1.41	2.45	32.30	7.84		no
1/4	49.20	22.90	1.60	2.23	16.80	7.27		no
1/6	50.50	25.20	1.65	2.14	13.20	7.31		no

the syntheses of these polymers, the ratio of PSS to zirconium *n*-butoxide was adjusted to give the same Si/Zr ratio ((total Si)/Zr=100/1) in the products. The Si/Zr ratio of the copolymers are found to be 99.7/1, 100.3/1, 100.2/1, and 99.7/1 for PSS/PHPS=2/1, 1/1, 1/4, and 1/6, respectively. The elemental analysis clearly shows the incorporation of the zirconium in the copolymers. The DSC result suggests that a certain amount of thermosetting units are necessary to render thermosetting property to the copolymer, even though the copolymer contained the bondings through zirconium *n*-butoxide. PHPS was essential (more than PSS/PHPS=1/1) to obtain copolymers with thermosetting property.

3.2 Conversion of the copolymers into silicon carbide-based ceramics

As shown in Fig. 4, the TGA curve of the copolymer (PSS/PHPS=1/4, (total Si)/Zr=100/1) indicates that the weight loss of the polymer starts around 100°C and is completed around 800°C in N₂. Two regions are apparent in the TGA curve. The first region, below 300°C, shows a weight loss of 2%, which results from the decomposition of the zirconium *n*-butoxide.³⁾ The second region, from 300 to 800°C, is thought to correspond to the breaking of organic bonds with the formation of gaseous species. The decomposition of PHPS is completed around 600°C.¹¹⁾ West et al. reported⁴⁾ that PSS shows weight loss due to evaporation of PhH, H₂, and CH₄, up to 800°C. The second region in the TGA curve up to 600°C is due to the decomposition of both PHPS and PSS blocks, while from 600 to 800°C is certainly due to the decomposition of PSS block.

Fig. 4. TGA of the copolymer (PSS/PHPS=1/4, (Total Si)/Zr=100/1) (N₂ flow : 100 cm³/min, heating rate : 5°C/min).

Table 2. Elemental Analysis and Rule-of-Mixtures Composition of Pyrolysis Products [(Total Si)/Zr=100/1] (N₂, 1500°C)

PSS/PHPS (Si ratio)	Composition (mass%)						Rule-of-mixtures composition (moles relative to SiC)					
	Si	N	Zr	O	C	H	ZrC	SiO ₂	Si ₃ N ₄	SiC	C	
1/1	53.50	14.00	1.73	2.94	27.20	0.70	0.018	0.086	0.21	1	1.1	
1/4	58.30	18.20	1.98	2.64	18.20	0.70	0.021	0.08	0.32	1	0.46	
1/6	61.00	20.20	2.02	2.60	13.60	0.60	0.022	0.079	0.35	1	0.09	
PSS	48.30	1.80	—	1.80	47.40	0.70	—	0.036	0.02	1	1.5	

The results of the elemental analysis of pyrolyzed samples are shown in Table 2. The nitrogen content in the ceramics are decreased in comparison with those in the polymers. Nitrogen has given off during the pyrolysis process, as expected from thermodynamic point of view.¹³⁾ Nitrogen in the pyrolyzed PSS was introduced during the pyrolysis in N₂ atmosphere. Rule-of-mixtures compositions are calculated by assigning all O to Si as SiO₂; all N to Si as Si₃N₄; all Zr to C as ZrC; then all C to Si as SiC; excess C or Si is assumed to be in the elemental state.¹⁴⁾ Molar ratios, normalized to SiC, are shown in Table 2. Ceramics derived from PSS/PHPS=1/4 contains small amount of elemental carbon, compared with that in pyrolyzed PSS. PHPS is excess in Si, relating to Si₃N₄. Elemental Si is formed by pyrolysis in N₂ because nitrogen has given off. Elemental Si from PHPS compensates elemental C from PSS. Free C in the final ceramics can be reduced by varying ratio of PSS/PHPS.

XRD patterns of the pyrolyzed copolymers (PSS/PHPS=1/1, 1/4, and 1/6, (total Si)/Zr=100/1) are shown in Fig. 5. Ceramics derived from PSS/PHPS=1/1 shows a broad pattern characteristic of β -SiC of small crystallite size with a broad peak around 25° which is assigned to C with poor crystallinity. Pyrolyzed PSS/PHPS=1/4 exhibits broad pattern characteristic of β -SiC of small crystallite size with broad peak at 25°. The broad peak at 25° is smaller than that of the pyrolyzed PSS/PHPS=1/1. It is consistent with the amount of excess carbon based on rule-of-mixture compositions. Ceramics from PSS/PHPS=1/6 shows patterns of α -Si₃N₄ on the halo of β -SiC and C. Excess carbon, based on rule-of-mixture compositions, is present in ceramics from PSS/PHPS=1/6. However, crystallization of α -Si₃N₄ has proceeded. This indicates that some carbon precursors in the copolymer are stable and do not react with Si. Above 800°C, aromatics are the most stable hydrocarbons. The formation of aromatics from methyl radical, derived from methyl groups of PSS, can take place by way of formation of

Fig. 5. X-ray diffraction patterns of pyrolyzed copolymers (A) PSS/PHPS=1/1, (B) PSS/PHPS=1/4, and (C) PSS/PHPS=1/6 (N₂, 1500°C).

hydrocarbons having a greater number of carbon atoms, formation of double bond, and Diels–Alder reactions.¹⁵⁾ During these multistage reactions, reactive species might react with Si and form Si–C bond. On the other hand, phenyl radical, derived from phenyl groups of PSS, might form biphenyl. Heat treatment of biphenyl leads to planar multiple ring structures, which is thought to be detected as C with poor crystallinity by XRD. Certain amount of free carbon should be formed if we try to suppress the crystallization of α -Si₃N₄ in the ceramics derived from PSS/PHPS at 1500°C in N₂.

3.3 Properties of ceramic fiber

Copolymer of PSS/PHPS=1/4 ((total Si)/Zr=100/1) is thermosetting and derived ceramics is amorphous. This copolymer was chosen to prepare a ceramic fiber.

Black shiny ceramic fiber with a diameter in the range of 10 to 12 μ m was obtained. The fiber contains 57.1 mass% Si, 14.2 mass% N, 18.8 mass% C, 8.09 mass% O, and 1.86 mass% Zr. Increase of oxygen content, in comparison with that of pyrolyzed powder, is due to oxygen inadvertently introduced during the spinning and handling steps. Tensile strength and elastic modulus measured for this fiber

were σ =1.0 GPa and E =190 GPa. The fractograph (Fig. 6) showed a typical feature of tensile fracture of brittle materials. Crystallite was observed on the surface of the fiber. XRD pattern reveals the mixture of small crystallite β -SiC with poor crystallinity C. Crystalline phase of the crystallite on the surface of the fiber could not be identified by XRD. However, low tensile strength of the fiber should be due to the crystallite which is thought to be a fracture origin. XPS analysis was performed on ground ceramic fiber. Figure 7 shows a plot of XPS binding energy for the fiber. A deconvolution analysis of the result shows that the Si 2p peak is composed of three components; Si–O (103 eV), Si–C (101 eV), and an intermediate one (102 eV). Si–N has a binding energy of 102 eV. The fiber contains 14.2 mass% of nitrogen, and the signal at 102 eV can be assigned to mixture of Si–N with O–Si–C species. C 1s signal is composed of two components; Si–C (283 eV) and C (285 eV). This spectrum corroborates the existence of free carbon. Zr 3d signal is composed of four components; spin doublet 3d_{1/2}–3d_{3/2} assigned to Zr–O (180 eV, 3d_{3/2}) and O–Zr–C (182 eV, 3d_{3/2}). The fiber displays features of Si–C with minor amount of Si–N, O–Si–C, Si–O, Zr–O, O–Zr–C, and free carbon.

For the elucidation of the crystallization behavior, the fiber was annealed in N₂ at 1700°C for 1h. Weight loss of 13% was observed and the fiber turned green in color. XRD indicated the presence of crystalline α -Si₃N₄, β -Si₃N₄, and β -SiC (Fig. 8). There was no peak assigned to ZrO₂ or ZrC. However, small peaks of ZrN were observed. ZrN can be formed by the reaction of Zr–O with free carbon and atmospheric nitrogen. The annealed fiber possessed a porous, large-grained crystalline structure and was too weak to conduct tensile strength measurement.

Fig. 6. Fracture surface of PSS/zirconium *n*-butoxide/PHPS derived fiber (N₂, 1500°C).

Fig. 7. XPS spectra of PSS/zirconium *n*-butoxide/PHPS derived fiber (A) Si 2p, (B) C 1s, and (C) Zr 3d.

Fig. 8. X-ray diffraction pattern of ceramic fiber derived from PSS/zirconium *n*-butoxide/PHPS annealed in N_2 at 1700°C for 1h.

4. Conclusion

Copolymer of PSS and PHPS was obtained by reacting PSS with zirconium *n*-butoxide and PHPS. Zirconium *n*-butoxide and PHPS (more than PSS/PHPS=1/1) were essential for the polymer to show thermosetting property. The thermosetting copolymers were converted into silicon carbide-based ceramics by pyrolysis in a stream of N_2 to 1000°C with about 80 mass% ceramic yield. The main phase of the pyrolysis product at 1500°C in N_2 was small crystallite β -SiC. Free carbon, based on rule-of-mixtures composition, in the final ceramics could be reduced by varying the ratio of PSS/PHPS.

The copolymer (PSS/PHPS=1/4, (total Si)/Zr=100/1) was dry spun and pyrolyzed to produce ceramic fiber. Pyrolysis in N_2 to 1500°C yielded a silicon

carbide-based fiber. Tensile strength of 1.0 GPa and elastic modulus of 190 GPa were obtained for the fiber which ranged from 10 to 12 μm in diameter. Crystallization to α -Si $_3$ N $_4$, β -Si $_3$ N $_4$, β -SiC, and ZrN proceeded on annealing in N_2 at 1700°C for 1h.

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